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NOTE ON PHASE SPACE CONTRACTION AND ENTROPY PRODUCTION IN THERMOSTATTED HAMILTONIAN SYSTEMS

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Abstract

The phase space contraction and the entropy production rates of Hamiltonian systems in an external field, thermostatted to obtain a stationary state are considered. While for stationary states with a constant kinetic energy the two rates are formally equal for all numbers of particles N, for stationary states with constant total (kinetic and potential) energy this only obtains for large N. However, in both cases a large number of particles is required to obtain equality with the entropy production rate of Irreversible Thermodynamics. Consequences of this for the positivity of the transport coefficients and for the Onsager relations are discussed. Numerical results are presented for the special case of the Lorentz gas.

1 Introduction

In the last decade or so, important new connections have been made between the mathematical theory of dynamical systems and the statistical mechanics of systems in nonequilibrium stationary states. In particular, the average phase space contraction rate of a dissipative dynamical system was equated to the physical entropy production rate as given by Irreversible Thermodynamics. This has also led to apparent contradictions between the mathematical theorems established on the basis of dynamical systems theory and the lore of statistical mechanics about irreversibility. The purpose of this paper is to reconcile these apparently contrasting results.

For instance, the proof that the entropy production rate[1] in a dynamical system in a nonequilibrium stationary state is necessarily positive [1] (see also Refs.[2, 3]), would imply that certain transport

[1]We should rather say *generalized* entropy production, because the stationary states we consider may be quite far from equilibrium. We will not do this, in order to simplify the language, so *generalized* should be understood where appropriate.

coefficients are also positive, in accordance with the Second Law of Thermodynamics. In other words, the Law could be directly verified for such a dynamical system. Because the proof in Ref.[1] only needs the system to be strongly chaotic and dissipative, with no vanishing Lyapunov exponents, it appears that the number of particles N plays no role in the derivation of the Second Law. This contradicts one of the basic tenets of statistical mechanics, which attributes the Second Law of Thermodynamics to the very large number of particles present in macroscopic systems.[2]

Similarly, Ref.[4] gives a proof the validity of Onsager reciprocal relations (OR), and explicitly states that the proof is valid for any number of particles. This is at least in appearance at variance with Onsager's derivation of the OR, where he considers macroscopic systems containing a sufficiently large number of particles, that they can be subdivided into subsystems, still containing a very large number of particles (see Refs.[3, 5, 6] for other recent derivations of the OR).

In this paper, we will attempt to reconcile these apparent paradoxes, along, in fact, similar lines as Boltzmann tried to reconcile Zermelo's recurrence paradox, based on Poincaré's recurrence theorem for dynamical systems, with his own results for the approach to equilibrium, based on the H-theorem. The main point here is to distinguish between mathematical correctness and physical relevance. There is no question that the results mentioned above, and others as well, which are solely based on the strong chaoticity of the relevant dynamical systems, are correct. However, in this paper we argue that they acquire physical significance only when they pertain to "macroscopic" systems, i.e. to dynamical systems with many degrees of freedom, representing the dynamics of a large number of particles.

To make this idea more precise, we focus on a special class of systems consisting of N particles in a d dimensional space, whose coordinates and momenta are denoted respectively by $\mathbf{q} = \{\mathbf{q}_i\}_{i=1}^N$, and $\mathbf{p} = \{\mathbf{p}_i\}_{i=1}^N$. The relevant phase space is taken to be $\Omega \subset I\!R^{2dN}$ and a point $\Gamma \in \Omega$ represents a possible phase for the system. Where appropriate we use $(\mathbf{q}, \mathbf{p})$ to represent a point in Ω. In general, the phase of the system changes in time defining an evolution in Ω, which we represent by the one paramter group of transformations $S^t : \Omega \to \Omega$, such that $S^t\Gamma$ is the phase of the system at the time $t \in I\!R$, if the initial phase is Γ ($S^0\Gamma = \Gamma$). The special class of dynamical systems of this form that we consider are the isokinetic (IK) as well as the isoenergetic (IE) thermostatted Hamiltonian systems, to be described in Section 2. A dynamical system of this kind will be called "macroscopic" if N is sufficiently large that its properties can also be observed in physical systems, i.e. in real experiments.[3]

The motivation for saying that the properties of such systems have a physical meaning only for large N is at least two-fold. In the first place, it should be borne in mind that physical (measurable) quantities are defined by time averages, such that the measured quantity corresponding to a phase variable A is given by

$$\bar{A}(\Gamma) = \lim_{T\to\infty} A_T(\Gamma) \ , \quad A_T(\Gamma) \equiv \frac{1}{T}\int_0^T A(S^\tau\Gamma)d\tau \ . \tag{1}$$

If one considers a class of sufficiently regular functions A, the notion of ergodicity can be introduced, which implies the existence of a probability measure μ on Ω such that $\bar{A}(\Gamma) = \langle A\rangle$ for almost all

[2] A similar argument was used in the context of Hamiltonian systems by J.L. Lebowitz in *Boltzmann's entropy and time's arrow*, Physics Today, September 1993, p.38. The paper ended with this statement: *This is an essential difference (unfortunately frequently overlooked or misunderstood) between the irreversible and the chaotic behavior of Hamiltonian systems. The latter, which can be observed already in systems consisting of only a few particles, will not have unidirectional time behavior in any particular realization. Thus if we had only a few hard spheres in a box, we would get plenty of chaotic dynamics and very good ergodic behavior, but we could not tell the time order of any sequence of snapshots.*

[3] One may be satisfied with the possibility of observing a given property in a numerical simulation. In this case, the property must become evident within a limited number of steps, also to prevent the numerical noise from overwhelming the measured quantity. For instance, the CPU time for a simulation of N non interacting particles for a time t may be the same as that for a simulation of $2N$ particles for a time $t/2$, but the numerical errors may be smaller in the second case. Hence higher N should still be preferred. More importantly, our point concerns physical times not the CPU times of computer experiments, even if these can be used in place of real experiments.

$\Gamma \in \Omega$, where

$$\langle A \rangle = \int_\Omega A(\Gamma) d\mu(\Gamma) \ . \tag{2}$$

The measure μ then represents the stationary state of the system, is S^t invariant, and is called natural (or physical) measure. The existence of such a measure is usually only assumed, because the cases of interest in statistical mechanics for which a proof has been given are very few (see Ref.[7] for a recent review on the subject). Thus, we also assume that the systems under consideration are ergodic. Secondly, however, the presence of a limit in T in Eq.(1) raises the question of which are the typical time scales of the system. In other words, one should be able to identify the time T that is needed in order for the difference between A_T and $\langle A \rangle$ to become a negligible quantity. This value of T is then the relaxation time of the system and to make physical sense this time should roughly be of the order of the physical times, which are the collision or interaction times, of the system. We say that a necessary condition for a system to be considered macroscopic (or physically relevant) is that its relaxation time remains within physical times. This view implies, in particular, that the equality of the average phase space contraction and entropy production rates used in the papers mentioned above may be physically relevant only for macroscopic systems, because only then will the relaxation times remain within physical times.

In Section 4. the paradigmatic case of a Lorentz gas is treated in detail, to give an example in support of the view that only a system consisting of many particles does, under general conditions, approach the infinite time limit sufficiently fast that its properties can be observed in experiments or, at least, in numerical simulations. In Section 2 and Section 3, we show that there is another reason for requiring that N be large. Indeed, the entropy production and the phase space contraction rates of the IE thermostatted Hamiltonian systems differ by terms of order $O(1/N)$. Thus, another necessary condition for a system to be considered physically relevant is that such terms are sufficiently small. In Section 5. a discussion of the results is given. In particular, in that section we point out the connection of our results with the problem of equivalence of ensembles in nonequilibrium statistical mechanics.

2 Thermostatted Hamiltonian systems

The equations of motion for a thermostatted Hamiltonian system in d-dimensional space are:

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} \ , \\ \dot{\mathbf{p}}_i &= -\frac{\partial}{\partial \mathbf{q}_i}\left[\Phi^{\rm int}(\mathbf{q}) + \Phi^{\rm ext}(\mathbf{q})\right] - \alpha(\Gamma)\mathbf{p}_i \\ &= \mathbf{F}_i^{\rm int}(\mathbf{q}) + \mathbf{F}_i^{\rm ext}(\mathbf{q}) - \alpha(\Gamma)\mathbf{p}_i \ , \quad i = 1, ..., N \ . \end{aligned} \tag{3}$$

where we assume that the N particles have the same mass m, $\Phi^{\rm int}(\mathbf{q})$ is the potential energy of the interactions among the particles and $\Phi^{\rm ext}(\mathbf{q})$ is the potential of the external fields of force doing work on the system. The gradients of such potentials give the forces acting on the particles, which we denote by $\mathbf{F}_i^{\rm int}(\mathbf{q})$ and $\mathbf{F}_i^{\rm ext}(\mathbf{q})$. The "friction" term, $-\alpha(\Gamma)\mathbf{p}_i$, represents a coupling with a thermostat, which allows the system to reach a stationary state, despite the presence of an external field of force.

The stationary state is usually obtained in one of two ways: either one imposes an isokinetic (IK) constraint, so that the total kinetic energy of the system $K = \sum_{i=1}^N \mathbf{p}_i^2/2m$ remains constant, or an isoenergetic (IE) constraint is imposed so that the total internal energy of the system $E = K + \Phi^{\rm int}$ remains constant. The two constraints result, in general, into two different stationary states. There are various ways of imposing that the equations of motion of our systems obey one or the other (non-holonomic) constraint. Here, we follow Gauss' principle of least constraint [8, 9], obtaining the

following expressions for the term α in Eqs.(3):

$$\alpha_{IK}(\Gamma) = \frac{\sum_{i=1}^{N} \mathbf{p}_i \cdot \left[\mathbf{F}_i^{\text{int}}(\mathbf{q}) + \mathbf{F}_i^{\text{ext}}(\mathbf{q})\right]}{\sum_{i=1}^{N} \mathbf{p}_i^2} \tag{4}$$

for the IK constraint and

$$\alpha_{IE}(\Gamma) = \frac{\sum_{i=1}^{N} \mathbf{p}_i \cdot \mathbf{F}_i^{\text{ext}}(\mathbf{q})}{\sum_{i=1}^{N} \mathbf{p}_i^2} \tag{5}$$

for the IE constraint, respectively. Substituting either Eq.(4) or Eq.(5) into Eqs.(3) assures that the stationary states will be characterized by a given kinetic or total energy as appropriate. Note that the presence of the constraint reduces the number of degrees of freedom from $2dN$, for the non-thermostatted Hamiltonian system, to $2dN-1$. We now compute for the systems given by Eqs.(3,4,5) the phase space contraction rate defined by:

$$\kappa_{IK}(\Gamma) \equiv -\frac{d}{d\Gamma} \cdot \dot{\Gamma} = -\sum_{i=1}^{N} \left[\frac{d}{d\mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{d}{d\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i\right] = (dN-1)\alpha_{IK}(\Gamma) \tag{6}$$

for the IK case, and

$$\kappa_{IE}(\Gamma) \equiv -\frac{d}{d\Gamma} \cdot \dot{\Gamma} = -\sum_{i=1}^{N} \left[\frac{d}{d\mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{d}{d\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i\right] = (dN-1)\alpha_{IE}(\Gamma) \tag{7}$$

for the IE case respectively. In these definitions, we have introduced a minus sign anticipating the positivity of α (on average) in the stationary state.

In order to compare the phase space contraction rates with the entropy production rates of Irreversible Thermodynamics, we first have to average the phase space contraction rates over the stationary state, so that they can be compared with macroscopic quantities. This leads to

$$\langle \kappa_{IK} \rangle_{ss} = (dN-1)\left[\left\langle \frac{\sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \mathbf{F}_i^{\text{int}}}{\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m}} \right\rangle_{ss} + \left\langle \frac{\sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \mathbf{F}_i^{\text{ext}}}{\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m}} \right\rangle_{ss}\right] \tag{8}$$

where we have divided numerator and denominator by the particles' mass m.

Noting that in the IK case one can define the stationary state temperature T_{ss} by:

$$\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} = \left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} \right\rangle_{ss} = (dN-1)k_B T_{ss} \tag{9}$$

and that

$$\sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \mathbf{F}_i^{\text{int}}(\mathbf{q}) = -\frac{d}{dt}\Phi^{\text{int}}(\mathbf{q}) \tag{10}$$

so that

$$-\left\langle \frac{d}{dt}\Phi^{\text{int}} \right\rangle_{ss} = -\frac{d}{dt}\left\langle \Phi^{\text{int}} \right\rangle_{ss} = 0 \tag{11}$$

we obtain:

$$\hat{\kappa}_{IK} \equiv \frac{\langle \kappa_{IK} \rangle_{ss}}{V} = \frac{\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i}{mV} \cdot \mathbf{F}_i^{\text{ext}} \right\rangle_{ss}}{k_B T_{ss}} \ . \tag{12}$$

Here, we have introduced $\hat{\kappa}_{IK}$, by dividing $\langle \kappa_{IK} \rangle_{ss}$ by the volume V of the system, in order to compare later dynamical averages with macroscopic thermodynamic quantities. Assuming for simplicity that $\mathbf{F}_i^{\rm ext}(\mathbf{q})$ is independent of i and $\mathbf{q}$: i.e. $\mathbf{F}_i^{\rm ext}(\mathbf{q})$ is the constant $\mathbf{F}^{\rm ext}$, and noting that

$$\frac{1}{V} \left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \right\rangle_{ss} \tag{13}$$

is just the particle current density $\mathbf{J}$, one obtains from (12)

$$\hat{\kappa}_{IK} = \frac{\mathbf{J} \cdot \mathbf{F}^{\rm ext}}{k_{_B} T_{ss}} \ . \tag{14}$$

Similarly, from Eqs.(5,7), one has for the IE case:

$$\hat{\kappa}_{IE} \equiv \frac{\langle \kappa_{IE} \rangle_{ss}}{V} = (dN - 1) \left\langle \frac{\sum_{i=1}^{N} \frac{\mathbf{p}_i}{mV} \cdot \mathbf{F}^{\rm ext}}{\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m}} \right\rangle_{ss} \tag{15}$$

However, now only for large N could the average of the ratio on the right hand side of (15) be replaced by the ratio of the averages, the latter being typical for macroscopic relations. Setting then in addition

$$\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} \right\rangle_{ss} = dN k_{_B} T_{ss} \tag{16}$$

and neglecting terms of order $1/N$ in the ratio $(dN-1)/dN$ as well, one obtains

$$\hat{\kappa}_{IE} = \frac{\mathbf{J} \cdot \mathbf{F}^{\rm ext}}{k_{_B} T_{ss}} \ . \tag{17}$$

The identity between the entropy production and phase space contraction rates per unit volume requires now that N be large.

3 Irreversible Thermodynamics

In order to compare the expressions for $\hat{\kappa}_{IK}$ and $\hat{\kappa}_{IE}$ with the corresponding entropy density production rate used in Irreversible Thermodynamics, we should first realize that in the latter case the system is supposed to be in first approximation in a (local) thermodynamic equilibrium state, where all extensive properties are proportional to N and depend further only on the temperature and the number density $n = N/V$. The entropy production rate per unit volume of Irreversible Thermodynamics is then that for the (adiabatic) Hamiltonian system defined by Eq.(3) with $\alpha(\Gamma) = 0$, and given by

$$\sigma = \frac{\mathbf{J} \cdot \mathbf{X}}{k_{_B} T_{ss}} \ . \tag{18}$$

Here, $\mathbf{J}$ is the macroscopic current density induced in the system by the external force $\mathbf{F}^{\rm ext}$, T_{ss} is the temperature of the stationary state and $\mathbf{X}$ is the thermodynamic force conjugate to the current density $\mathbf{J}$. One would like that the same expression holds both for the IK and IE cases, i.e. that

$$\sigma_{IK} = \sigma_{IE} = \sigma \tag{19}$$

holds. We consider the IK case first.

To compare (18) with quantities derivable from a Hamiltonian dynamical system, we assume that the thermodynamic force is like an, e.g. electric, field $\mathbf{E}$, that can be derived from an external potential. Identifying now in (12)

$$\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i}{mV} \cdot \mathbf{F}^{\rm ext} \right\rangle_{ss} = \mathbf{J} \cdot \mathbf{X} \tag{20}$$

where both sides of the equation give the work done on the system in the stationary state by the external force $\mathbf{F}^{\rm ext} = \mathbf{X}$ per unit volume and unit time, we see that (12,14) and (18) formally agree.

With a similar identification for (17) and (18), one also has a formal agreement between the two equations for the IE case, albeit that the large number of particles in the system had to be used to obtain this agreement.

4 The Lorentz gas − Color diffusion

In this section we use a simple model −the thermostatted Lorentz gas− to show that the formal agreement obtained between dynamical phase space contraction and entropy production rates of thermostatted Hamiltonian systems in nonequilibrium stationary states only has *physical* significance if the number of particles N of these systems is large. In fact, a new large N requirement comes in addition to that of the previous section and holds both for IK and IE systems. That is, that the relaxation times to obtain the observed macroscopic values of the physical properties of a system might be unphysically long for systems consisting of a small number of particles. As an illustration, we consider numerical results from the equilibrium Lorentz gas with periodic boundary conditions. The relevance of these results for nonequilibrium systems will be discussed at the end of this section and the beginning of next section (point 1).

The thermostatted Lorentz gas consists of one point particle of mass m, which moves through an array of fixed scatterers in the presence of a constant external field $\mathbf{E}$ driving the particle. We do not require the scatterers to be hard; they might be soft as in the model studied in Ref.[10]. For simplicity, we assume that the particle has a (color) charge c on which the field $\mathbf{E}$ acts. The equations of motion for the moving particle are then:

$$\begin{aligned} \dot{\mathbf{q}} &= \frac{\mathbf{p}}{m} \,, \\ \dot{\mathbf{p}} &= \mathbf{F}^{\rm int}(\mathbf{q}) + c\mathbf{E} - \alpha(\Gamma)\mathbf{p} \,, \end{aligned} \tag{21}$$

Here, $-\alpha(\Gamma)\mathbf{p}$ represents again a thermostat coupling needed to attain a stationary state for the moving particle, by balancing the continuous acceleration of the particle due to the external field $\mathbf{E}$ with an effective friction term.

If the scatterers are hard disks or hard spheres, as usually considered, there is no internal potential energy in the system and $\mathbf{F}^{\rm int}$ is a purely impulsive force, causing specular reflection of the particle from a scatterer. In that case, the IK constraint is the same as the IE constraint, and one has:

$$\alpha_{IK}(\Gamma) = \alpha_{IE}(\Gamma) = \frac{\mathbf{p} \cdot c\mathbf{E}}{\mathbf{p}^2} \,. \tag{22}$$

In general we have then:

$$\langle \kappa_{IK} \rangle_{ss} = \frac{\left\langle \mathbf{p} \cdot \left(\mathbf{F}^{\rm int} + c\mathbf{E} \right) / m \right\rangle_{ss}}{k_B T_{ss}} = \frac{\langle \mathbf{p} \cdot c\mathbf{E}/m \rangle_{ss}}{k_B T_{ss}} \tag{23}$$

where we have set $\mathbf{p}^2/m = \langle \mathbf{p}^2/m \rangle_{ss} = (d-1) k_B T_{ss}$ and used that $\langle \mathbf{p} \cdot \mathbf{F}^{\rm int} \rangle_{ss} = 0$, similarly to Eqs.(9,10). We note that the right hand side of Eq.(23) equals the entropy production rate.

On the other hand,

$$\langle \kappa_{IE} \rangle_{ss} = (d-1) \left\langle \frac{\mathbf{p} \cdot c\mathbf{E}/m}{\mathbf{p}^2/m} \right\rangle_{ss} \ . \tag{24}$$

Since there is only one moving particle, one cannot replace on the right hand side of (24) the average ratio by the ratio of the averages. If one nevertheless does so and sets $\langle \mathbf{p}^2/m \rangle_{ss} = dk_B T_{ss}$, one obtains the expression

$$\langle \kappa_{IE} \rangle_{ss} = \frac{d-1}{d} \frac{\langle c\mathbf{p}/m \rangle_{ss} \cdot \mathbf{E}}{k_B T_{ss}} \ , \tag{25}$$

which differs from the expected value of the entropy production rate of irreversible thermodynamics by an amount of

$$\frac{1}{d} \frac{\langle c\mathbf{p}/m \rangle_{ss} \cdot \mathbf{E}}{k_B T_{ss}} \ , \tag{26}$$

which is of the same order as $\langle \kappa_{IE} \rangle_{ss}$ itself.

The result of the above analysis is that for the IE Lorentz gas the average phase space contraction and the entropy production rates are not equal, while they are in the case of the IK Lorentz gas. At the same time, both the IE and the IK cases could be affected by the problem of unphysically long relaxation times.

Both difficulties can be overcome if many particles per unit volume are present in the system. Indeed, even non interacting particles would do, as the following three examples illustrate for the periodic (hard disk) Lorentz gas considered in Ref.[11]. In this case, there is an elementary cell (EC), whose copies tile the whole two dimensional plane, where each cell contains one fixed scatterer and one (or more) moving particles. Also, there are no external fields and thermostat couplings, so that this is an equilibrium system.

(a) In order to compute then the diffusion coefficient D of a point particle through the scatterers, we take a collection of N particles (initially uniformly distributed in each EC) $\{\mathbf{q}_i(0)\}_{i=1}^N$ and, similarly to what was done in [11], we let these particles evolve for a fixed time τ. Because of the periodic boundary conditions, the particle density equals N moving particles per EC at all times. Let us denote by $\mathbf{q}_i(\tau)$ the final position of the i-th particle trajectory and by $\mathbf{r}_i(\tau)$ the displacement $\mathbf{q}_i(\tau) - \mathbf{q}_i(0)$. The simulations yield a value $D_{\rm sim}$, which is related to D by

$$D_{\rm sim} \equiv \frac{\sum_{i=1}^N \mathbf{r}_i^2(\tau)}{N\tau} = D + \epsilon(N,\tau) \tag{27}$$

where $\epsilon(N,\tau)$ can be made arbitrarily small by taking sufficiently large N and τ.[4] Since for the Lorentz gas the many independent initial conditions also represent the members of an ensemble, the extrapolation to large N can be seen here as one in "ensemble size". In other words, taking the limit of large N in Eq.(27), amounts to reproducing the microcanonical ensemble average $\langle \mathbf{r}^2(\tau) \rangle$ for any fixed $\tau > 0$. How large does τ have to be for a given N, so that $|\epsilon(N,\tau)|$ is smaller than a given $\varepsilon > 0$? One finds that the larger N, the shorter τ can be (see Figure 1 and Table 1). In particular, for $N = 1$ no diffusive behaviour can be discerned at all in runs of 10^9 collisions. For larger N, instead, we see that $D_{\rm sim}$ values close to D are obtained: the quicker the larger N and the better the larger τ.[5] In the limit of very large N, diffusive behavior is then expected to become observable in times of about one collision time, i.e. the expected physical time.[6]

[4] The best numerical estimate for D given in Ref.[11] is $D_{\rm num} = 0.2492(3)$.

[5] This is qualitatively shown in Figure 1, where we have taken some special values of N. In Table 1 we also included intermediate values both for N and time, so that larger oscillations about the general trend are present.

[6] Here and in the following we mainly refer to the number of collisions per particle as a measure of the elapsed time, because the convergence of the time averages of the phase variables to the correct values is determined by this number. On the contrary, the actual values of the elapsed times have no special meaning by themselves since they depend on the scaling of the particle speed.

(b) The same kind of behavior is observed in the same equilibrium system for the internal potential part of the pressure defined by

$$p^{\Phi}V = -\lim_{T\to\infty}\frac{1}{T}\sum_{\text{collisions}}\mathbf{p}\cdot\hat{\mathbf{n}}\ . \tag{28}$$

Here the sum runs over all collisions between the N moving particles and the scatterers, which have taken place in the time T; $\mathbf{p}$ is the momentum of a colliding particle and $\hat{\mathbf{n}}$ is the outer normal to the scatterer at the collision point [9]. Our results are given in Figure 2, while the best numerical value for $p^{\Phi}V$ given in Ref.[11] is 0.5457(3). For a density of $N = 1$ particle per EC this value is obtained after 10^7 collisions.

(c) The third example we want to mention is obtained from the previous Lorentz gas system, in the limit that the spacing between the scatterers vanishes (the scatterers touch) and that there is only one moving particle per EC. This way each moving particle is confined inside a triangular like box, whose sides are arcs of three scatterer surfaces and we effectively simulate the dynamics of a *bona fide* 1-particle system in a box. This model was considered also in Ref.[11] for the calculation of the pressure (see the smallest value of V in Figure 3 in Ref.[11]). The result is that a number of about 10^7 collisions is necessary to obtain the value of the potential pressure with the same accuracy of example (b), by following the motion of the confined particle. The diffusion coefficient is obviously zero and was not computed.

The reason for a faster convergence of systems with larger N is obviously that more collisions take place in the same (physical) time. Hence, we believe that also nonequilibrium systems will behave in this fashion. The effect of the external fields present in molecular dynamics simulations is discussed in point 1 of the next section in the context of the thermostatted Lorentz gas.

5 Discussion

1. Our results indicate that there is no conflict between dynamical systems theory and Irreversible Thermodynamics. The entropy production rate of Irreversible Thermodynamics is only obtained from the phase space contraction rate of a dissipative IE dynamical system of N particles if terms of order $O(1/N)$ can be neglected, i.e. in the thermodynamic limit. The difficulty arises not only for the IE case, but also for the IK case, although a formal equality between the average phase space contraction and entropy production rates then holds for all N. Indeed, the time needed for the corresponding averages to be compared with the $\mathbf{J}\cdot\mathbf{X}$ of Irreversible Thermodynamics may be unphysically long if N is too small. Unfortunately, the modern methods of nonequilibrium molecular dynamics (NEMD) are not too helpful in this respect, not even for such a simple system as the Lorentz gas, because the fields then used are well beyond the linear regime.[7]

The problem to correctly simulate systems close to equilibrium by NEMD can be understood in terms of the model of Ref.[14]. In this model one moving particle, subject to a constant external field and a Gaussian thermostat, experiences elastic collisions with fixed circular scatterers, placed in a triangular lattice. First, we observe that reducing the field makes it more and more difficult to obtain the transport coefficient. This is illustrated in Figure 3 for the color conductivity L, defined as the time average of the color current J divided by the external field strength F_e. Secondly, reducing the

[7] This has been discussed, for instance, in pages 580-583 of Ref.[12] in the context of the van Kampen's objection to linear response theory [13]. Moreover, as pointed out also in Ref.[12], there may be regimes in which *"nonlinear corrections conspire to produce a linear effect with modified slope"*. The authors of Ref.[12], then add that this seems to be unlikely. However, it is consistent with the results of Ref.[14]. For instance, Figure 2 of that paper, shows a plateau in the conductivity as a function of field for large fields (around ≈ 0.4) which are already outside the linear regime. Hence, the observation of linear relations between thermodynamic forces and fluxes in NEMD does not necessarily mean effective observation of the linear regime of Irreversible Thermodynamics.

field also introduces larger errors in the calculation of the trajectory of the moving particle, so that a theoretical lower bound of about 10^{-6} for the field must be imposed. In reality, a combination of the times needed for the runs and for the precision that should be achieved, using double precision algorithms, imposes 10^{-4} as a lower bound for the field. At the same time, simple calculations show that a physical potential difference of 1 V/cm corresponds in our model to an unobtainable field strength of at most 10^{-6}, see also Ref.[12, 15]. Moreover, if one were to use the van Kampen argument [13] for the linear regime, then one should do simulations with $F_e \approx 10^{-35}$!

The question remains, in general, when dynamical systems results really correspond to those found for macroscopic systems. The possibly unphysically long times needed for small N to define the observed physical quantities as time averages makes then macroscopic concepts as temperature, pressure and their gradients (related to currents and thermodynamic forces), which occur in Irreversible Thermodynamics, questionable. This is even more relevant for thermostatted non-Hamiltonian systems, such as the SLLOD equations, which describe viscous flows (see Ref.[9]).

2. The necessity for the presence of many particles to obtain macroscopic behavior has been illustrated in terms of our results for the periodic Lorentz gas. We observed that diffusion and potential pressure both reach their correct average values within short times if the system has a suffcient number of particles per EC. If, to the contrary, N is small, large fluctuations have to be averaged out in the evolution of just the few particles present, which may take unphysically long times. From the mathematical point of view, instead, there is no problem because the time is then allowed to grow without bounds. In this sense, there is a similarity between the problem we addressed here and that posed by Poincaré's recurrence theorem and Boltzmann's H-theorem.

We remark that it is not clear to us what precise role chaoticity plays in obtaining macroscopic behavior of the properties of the system, as defined by time averages. While the presence of many particles per unit volume is clearly necessary, the degree of chaoticity needed to obtain physical behavior in physical times is unclear. That is, it remains an open question to identify the precise conditions on the interactions among the particles in the system −which imply then a given degree of chaoticity− so that physical behavior is obtained in physical times. We note that for ensemble averages to describe the properties of the system, a spreading of the ensemble in time is usually necessary, which also requires a certain degree of chaoticity of the system (see e.g. Ref.[16]). Indeed, in the cases we investigated it is observed that the time average reaches a good value when also the ensemble of trajectories has covered enough of the phase space.

3. Nevertheless, the theorems proved in Refs.[1, 4] for any number of particles imply important new insights. In particular, in view of the fact that Ruelle [1] uses effectively the phase space contraction rate, his theorem on the positivity of the average phase space contraction rate is not restricted, due to its dynamical nature, to systems close to equilibrium. Therefore, its applicability to macroscopic systems could imply the positivity of the transport coefficients also far from equilibrium, at least as long as there is strong chaoticity and no vanishing Lyapunov exponents. This then could lead to a proof of the positivity of the rheological viscosity of a fluid, i.e., the shear rate dependent viscosity of a fluid under shear far from equilibrium, not just for the (hydrodynamic) Newtonian viscosity of a fluid near equilibrium. Similarly, the cited proof of the Onsager reciprocal relations [4] seems really a proof of certain symmetry properties of the phase space contraction rates of a given class of dynamical systems. Hence, they constitute an example of mathematical results which, without physical motivation, would probably never have been considered in the context of dynamical systems. However, for large N, these mathematical results also have physical meaning.

4. Our arguments on the relevance of time scales in the IE and IK models is further strengthened by the recent results of Ref.[17], for the Fermi-Pasta-Ulam problem. There, it is shown that for sufficiently low energies there can be regions of phase space with positive measure, in which the transient behavior persists for arbitrarily large times and no equipartition of energy between the degrees of freedom of the system is observed. However, lower and lower energies are needed for these regions to exist as N

grows. Thus, the growing of N ensures that relaxation to the thermodynamic behavior takes place within physical time scales.

5. There is an additional reason why the number of degrees of freedom plays a role in the IK models. Consider one point particle in a one-dimensional space, with singular potential barriers, e.g. let the potential energy be $\Phi(x) = 1/|x|$. The equations of motion are then

$$\dot{x} = \frac{p}{m} \; ; \quad \dot{p} = \frac{1}{x|x|} + F - \alpha p \tag{29}$$

where $\alpha p = F + 1/x|x|$ and F is the force due to a constant external field. But this means that

$$\dot{x} = \frac{p}{m} \; ; \quad \dot{p} = 0 \tag{30}$$

which is trivially solved to give $x(t) = p(0)t/m + x(0)$. Therefore, the particle can move *through* a singularity of the potential, if the signs of $x(0)$ and $p(0)$ are opposite. More generally, the IK models can in principle allow arbitrarily large values of the total energy, because the thermostat can do any required amount of work on the system, in order to keep the kinetic energy constant. This fact does not constitute a problem for the average quantities, if the isokinetic distribution of Ref.[9] holds: in that case, the regions close to the singularities are given a weight which decreases exponentially with the potential energy, under the assumption that terms of order $O(1/N)$ can be neglected (cf. Ref.[9], Eqs.(5.25-5.28)).

6. Our comments do not imply that the study of low dimensional systems has no physical relevance from the point of view of transport theory. There are many reasons why low dimensional dynamical systems may correctly describe a given physical situation. For instance, one could model by a dynamical system only the macroscopic behavior, like, e.g., in hydrodynamics. In that case only a few variables will play a significant role for most physical situations. Also, recent studies show (see, e.g., Refs.[18, 19]) that the dynamics of chains of low-dimensional maps can be consistent with macroscopic transport equations, if there are many copies of the same map in the chain, i.e. if the thermodynamic limit is taken in that sense.

7. Our arguments are relevant also for the problem of equivalence of ensembles in nonequilibrium statistical mechanics. In particular, the idea that there may be several stationary distributions which become equivalent in the thermodynamic limit, is here confirmed by the fact that both the IK and the IE dynamics give rise to stationary states with the same entropy production rates for $N \to \infty$. Similarly to Refs.[19], also here the equivalence is based on the equality of entropy production rates, which determine the transport properties of the physical systems. The idea of the equivalence of nonequilibrium ensembles is rather new and has been discussed earlier from a variety of point of views in Refs.[19, 20].

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Figure captions

Figure 1. Diffusion coefficient $D_{\rm sim}$ for the periodic (triangular) Lorentz gas with an interdisk surface to surface spacing of $w = 0.3$, and disk radius of $r = 1$. The particle speed is also 1. The various curves correspond to different ensembles made up of N initially uniformly distributed members. The horizontal axis represents the average number of collisions per particle, for each ensemble. For $N = 4$ ($\diamond$) we see no convergence towards the value $D = 0.2492$. For $N = 32$ ($+$) convergence appears after 10^7 collisions. For $N = 152520$ ($\Box$) convergence takes place between 10 and 100 collisions. For $N \to \infty$, convergence is then expected to occur after about 1 collision.

Figure 2. Potential pressure for the periodic (triangular) Lorentz gas of Figure 1. The various curves correspond to different ensembles made of N members. The horizontal axis represents the average number of collisions per particle for each ensemble. Clearly, all curves converge to the numerically estimated value of 0.5457 (cf. Ref.[11]) represented by the dotted horizontal line, but the convergence is faster for larger N.

Figure 3. Here we see that the time it takes for the color conductivity L in the periodic, nonequilibrium Lorentz gas to reach its average value increases as the field strength F_e is decreased. For $F_e = 1$, convergence to 0.165 is obtained rather quickly, while for a field $F_e = 0.01$ large fluctuations survive at relatively long times. One should note that even our smallest field is much outside the linear regime, which is below field strengths of 10^{-6}.

Table captions

Table 1. Values of $\epsilon(N, \tau) = D_{\rm sim} - D$, Eq.(27), for the Lorentz gas of Figure 1 and for ensembles not represented in that figure. The first column represents the time τ elapsed for each initial condition at the moment when Eq.(27) is evaluated, while the remaining columns refer to ensembles with N initially uniformly distributed members. For D we have used the best numerical value $D_{\rm num} = 0.2492$ given in Ref.[11]. The units are such that the radius of the scatterers, the particle speed and mass are 1, while the distance between the centers of two nearest neighbor scatterers is 2.3. This table can also be used to choose N and τ to get a desired accuracy. The actual values of the time are not important: only the relative times are, because the time units depend on the velocity scaling.

Table 1

time	N=8	N=56	N=456	N=5740	N=45240	106250
2	-0.24566	-0.06059	-0.07124	-0.06192	-0.06692	-0.06667
32	-0.09114	0.01166	-0.02489	-0.00916	-0.00911	-0.00505
128	-0.13363	-0.01238	-0.01449	0.00004	-0.00148	-0.00161
8192	-0.00495	-0.03573	0.00630	-0.00331	-0.00049	-0.00166
16384	-0.09726	-0.04374	0.01165	0.00121	-0.00134	-0.00135

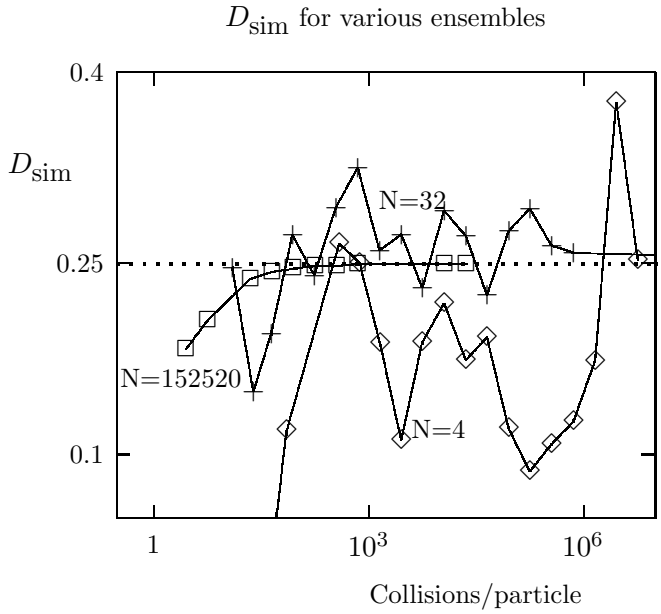

Figure 1

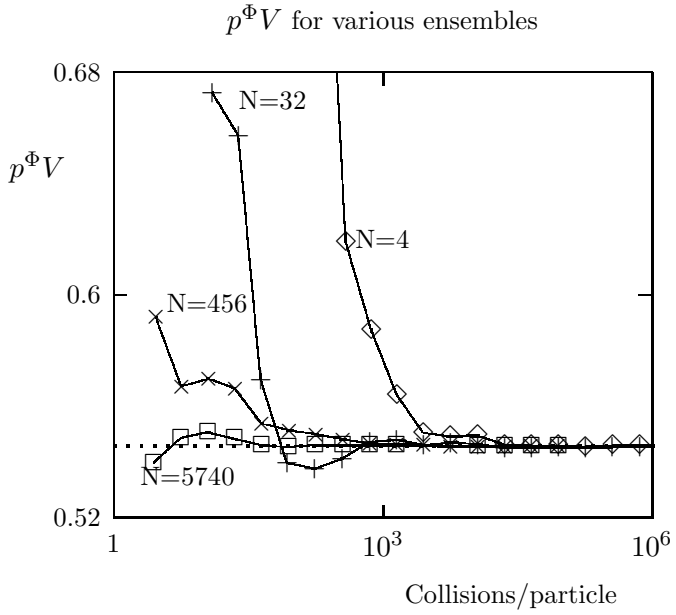
$p^{\Phi}V$ for various ensembles
0.68
0.6
0.52
$p^{\Phi}V$
N=32
N=4
N=456
N=5740
1
10^3
10^6
Collisions/particle

Figure 2

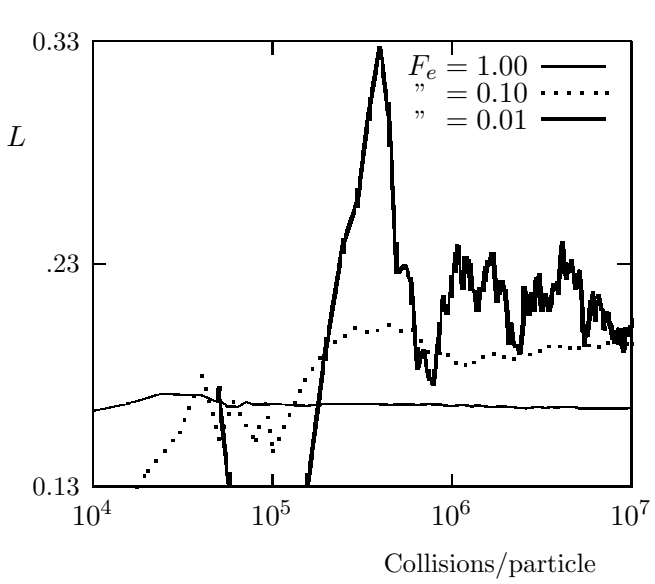
L for various fields
0.33
L
.23
0.13
$F_e = 1.00$
" $= 0.10$
" $= 0.01$
10^4
10^5
10^6
10^7
Collisions/particle

Figure 3